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(54) **Refrigerating machine oil composition**

Ölzusammensetzung für Kühlmaschine

Composition huileuse pour machines réfrigérantes

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(73) Proprietor: **IDEMITSU KOSAN CO., LTD.**
Tokyo 100-8321 (JP)

(72) Inventors:
• **SAKANOUÉ, Shuichi**
Chiba, Chiba 299-0107 (JP)
• **TAKESUE, Masahiko**
Chiba, Chiba 299-0107 (JP)

- **JIDO, Youichiro**
Chiba, Chiba 299-0107 (JP)
- **TAKAGI, Minoru**
Tokyo, Tokyo 100-8321 (JP)
- **TOMINAGA, Shoichi**
Tokyo, Tokyo 100-8321 (JP)
- **NAGAKAWA, Hiroshi**
Chiba, Chiba 299-0107 (JP)

(74) Representative: **Gille Hrabal Struck Neidlein Prop**
Roos
Patentanwälte
Brucknerstrasse 20
40593 Düsseldorf (DE)

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EP-A- 0 714 974 EP-A- 0 786 510
EP-A- 0 861 883 WO-A-93/01249
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DescriptionTECHNICAL FIELD

[0001] The present invention relates to a refrigerator oil composition. More precisely, it relates to a refrigerator oil composition of good lubricity, which is especially effective for reducing the friction and abrasion in both the oil region and the extreme-pressure region in the sliding area between aluminium materials and steel materials and which is favorable to lubricating oil for refrigerators using non-chlorine Flon refrigerants such as R134a and the like that do not bring about environmental pollution.

BACKGROUND ART

[0002] In general, a compressor-type refrigerator comprises at least a compressor, a condenser, an expansion mechanism (expansion valve, etc.), an evaporator and a drier, and a mixed liquid comprising a refrigerant and a lubricating oil is circulated in the closed system of the refrigerator. In the compressor-type refrigerator of that type, in general, dichlorodifluoromethane (R12), chlorodifluoromethane (R22) and the like have heretofore been used as refrigerants and various mineral oils and synthetic oils as lubricating oils.

[0003] However, since R12 and R22 will bring about environmental pollution, as destroying the ozone layer existing in the stratosphere, their use is being severely controlled in all the world. Given the situation, new refrigerants, non-chlorine Flon compounds such as hydrofluorocarbons have become specifically noted. Since such non-chlorine Flon compounds, for example, hydrofluorocarbons such as typically R134a will not destroy the ozone layer and can be substituted for R12 and the like without almost changing or modifying the structure of conventional refrigerators, they are favorable for refrigerants for compressor-type refrigerators.

[0004] The properties of these new Flon-substituent refrigerants are different from those of conventional Flon refrigerants; and it is known that refrigerator oils capable of being used along with these comprise a base oil component selected from, for example, polyalkylene glycols, polyesters, polyol esters, polycarbonates, polyvinyl ethers and alkylbenzenes having particular structures, and various additives added to the base oil component.

[0005] However, these refrigerator oils are seriously problematic in practical use in that, when used in the atmosphere comprising any of the above-mentioned refrigerants, their lubricity is poor and, in particular, they cause increased abrasion loss between aluminium materials and steel materials constituting compressors for air-conditioning refrigerators. Rotary-type, scroll-type and reciprocation-type compressors are used for air-conditioning refrigerators, and they have sliding members of a combination of aluminium materials and steel materials. In rotary-type compressors, for example, the bearing is the sliding member; in scroll-type compressors, the Oldham's coupling ring is the member; and in reciprocation-type compressors, the con'rod (aluminium)/piston pin (steel) member is the member. Regarding their condition for lubrication, the bearing and the Oldham's coupling ring act in an area which shall bear relatively low stress and in which the lubricating oil used exhibits its oily effect (this area is hereinafter referred to as an oil region); while the con'rod/piston pin member acts in an area which shall bear relatively high stress and which therefore requires the extreme-pressure effect of the lubricating oil used therein (this area is hereinafter referred to as an extreme-pressure region). In that situation, desired are refrigerator oils usable in any and every type of compressors, to which, therefore, desired are additives effective for reducing friction and abrasion in both regions, the oil region and extreme-pressure region.

[0006] For lubricity improvers for refrigerator oils, heretofore known are orthophosphates such as tricresyl phosphate (hereinafter referred to as TCP), triphenyl phosphate (hereinafter referred to as TPP), etc. These additives are effective for sliding members of a combination of steel materials and steel materials, but are not for those of a combination of steel materials and aluminium materials since they do not have the ability to reduce friction in the extreme-pressure region. Therefore, for ensuring good lubricity around them, the steel-aluminium sliding members require extreme-pressure agents substitutable for the conventional lubricity-improving additives.

[0007] On the other hand, another lubricity improver, sorbitan mono-oleate is proposed. This is effective for reducing friction in the oil region, but is problematic in that its volume resistivity is low.

[0008] The present invention has been made from the viewpoint as above, and its object is to provide a refrigerator oil composition of good lubricity, which is especially effective for reducing the friction in both the oil region and the extreme-pressure region in the sliding area between aluminium materials and steel materials and which is favorable to lubricating oil for refrigerators using non-chlorine Flon refrigerants such as R134a and the like that do not bring about environmental pollution.

[0009] European patent application EP -A- 0 714 974 describes oil compositions on the basis of a genetically modified oil or a synthetic triglyceride oil according to the formula at page 7, lines 26-42, of the document. This base oil of the oil composition is not a polyvinyl ether.

[0010] In WO -A- 93 01249 oil compositions on the basis of polyol esters are described. The base oil of the oil composition described in the document is not a polyvinyl ether either.

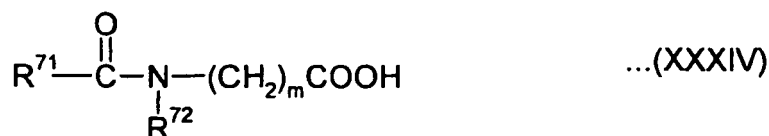
[0011] European patent application EP -A- 0 861 883 describes the use of polyvinyl ethers in refrigerator oil compositions, but does not teach the presence of the specific organic acid according to the present invention, or of a fatty acid amide.

DISCLOSURE OF THE INVENTION

[0012] We, the present inventors have assiduously studied so as to attain the object as above, and, as a result, have found that the object of the invention can be effectively attained by using specific additives. On the basis of this finding, we have completed the present invention.

[0013] The invention is summarized as follows:

- (1) A refrigerator oil composition comprising as a base oil at least one oxygen-containing synthetic oil, and containing (a) at least one organic acid of the following formula (XXXIV):

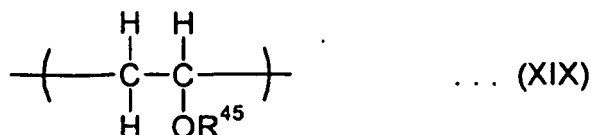


wherein R^{71} represents an alkyl group having from 6 to 30 carbon atoms, or an alkenyl group having from 6 to 30 carbon atoms; R^{72} represents an alkyl group having from 1 to 4 carbon atoms; and m represents an integer of from 1 to 4, or (b) at least one fatty acid amide,

wherein the oxygen-containing synthetic oil is a polyvinyl ether.

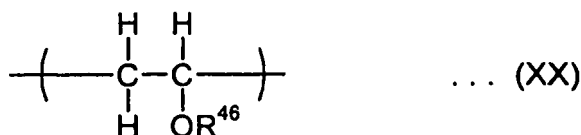
- (2) The refrigerator oil composition of above (1), wherein the amount of the components (a) or (b) falls between 0.01 and 5 % by weight based on the total amount of the composition.

- (3) The refrigerator oil composition of above (1), wherein the polyvinyl ether is a polyvinyl ether copolymer having constitutive units (A) of the following general formula (XIX)



wherein R^{45} represents a hydrocarbon group having from 1 to 3 carbon atoms and optionally an ether bond in the molecule,

and constitutive units (B) of the following general formula (XX)



wherein R^{46} represents a hydrocarbon group having from 3 to 20 carbon atoms and optionally an ether bond in the molecule, in which, however, R^{45} in the constitutive units (A) is not the same as R^{46} in the constitutive units (B).

- (4) The refrigerator oil composition of above (3), wherein R^{45} in the constitutive units (A) is an ethyl group, and R^{46} in the constitutive units (B) is an isobutyl group.

BEST MODES OF CARRYING OUT THE INVENTION

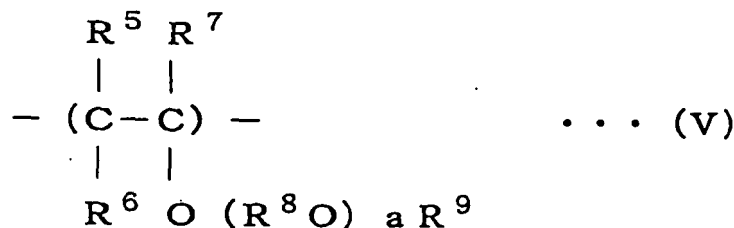
[0014] Embodiments of the invention are described below.

[0015] In the refrigerator oil composition of the invention, the base oil is an oxygen containing oil. Preferably, it has a kinematic viscosity at 40°C of from 2 to 500 mm²/sec, more preferably from 5 to 200 mm²/sec, even more preferably

from 10 to 100 mm²/sec. Its pour point that indicates the low-temperature flowability of the base oil is preferably not higher than -10°C.

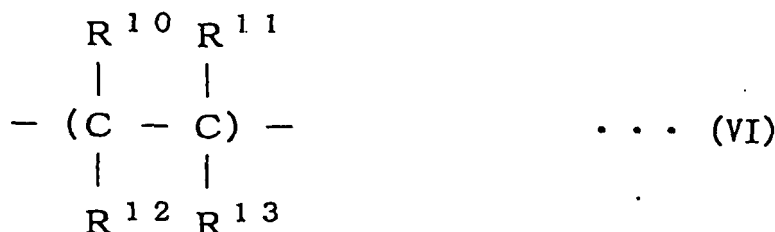
[0016] The oxygen-containing synthetic oil which is used in the invention is a polyvinyl ether.

[0017] The polyvinyl ether mentioned above includes, for example, polyvinyl ether compounds (1) having constitutive units of the following general formula (V):



wherein R⁵ to R⁷ each represent a hydrogen atom, or a hydrocarbon group having from 1 to 8 carbon atoms, and they may be the same or different; R⁸ represents a divalent hydrocarbon group having from 1 to 10 carbon atoms, or a divalent, ether bond oxygen-containing hydrocarbon group having from 2 to 20 carbon atoms; R⁹ represents a hydrocarbon group having from 1 to 20 carbon atoms; a represents a number of from 0 to 10 on average; R⁵ to R⁹ may be the same or different in different constitutive units; and plural R⁸O's, if any, may be the same or different.

[0018] Also usable herein are polyvinyl ether compounds (2) of block or random copolymers having constitutive units of formula (V) noted above and constitutive units of the following general formula (VI):



wherein R¹⁰ to R¹³ each represent a hydrogen atom, or a hydrocarbon group having from 1 to 20 carbon atoms, and they may be the same or different; and R¹⁰ to R¹³ may be the same or different in different constitutive units.

[0019] Further usable herein are polyvinyl ether compounds (3) that are mixtures of the above-mentioned polyvinyl ether compounds (1) and polyvinyl ether compounds (2).

[0020] In formula (V), R⁵ to R⁷ each represent a hydrogen atom, or a hydrocarbon group having from 1 to 8 carbon atoms, preferably from 1 to 4 carbon atoms. Concretely, the hydrocarbon group indicates, for example, an alkyl group including a methyl group, an ethyl group, an n-propyl group, an isopropyl group, all types of butyl group, all types of pentyl group, all types of hexyl group, all types of heptyl group, all types of octyl group; a cycloalkyl group including a cyclopentyl group, a cyclohexyl group, all types of methylcyclohexyl group, all types of ethylcyclohexyl group, all types of dimethylcyclohexyl group, etc.; an aryl group including a phenyl group, all types of methylphenyl group, all types of ethylphenyl group, all types of dimethylphenyl group; or an arylalkyl group including a benzyl group, all types of phenylethyl group, all types of methylbenzyl group. Especially preferably, R⁵ to R⁷ are hydrogen atoms.

[0021] In formula (V), R⁸ represents a divalent hydrocarbon group having from 1 to 10 carbon atoms, preferably from 2 to 10 carbon atoms, or a divalent, ether bond oxygen-containing hydrocarbon group having from 2 to 20 carbon atoms. Concretely, the divalent hydrocarbon group having from 1 to 10 carbon atoms indicates, for example, a divalent aliphatic group including a methylene group, an ethylene group, a phenylethylene group, a 1,2-propylene group, a 2-phenyl-1,2-propylene group, a 1,3-propylene group, all types of butylene group, all types of pentylene group, all types of hexylene group, all types of heptylene group, all types of octylene group, all types of nonylene group, all types of decylene group; an alicyclic group with two bonding sites to be derived from an alicyclic hydrocarbon which includes cyclohexane, methylcyclohexane, ethylcyclohexane, dimethylcyclohexane, propylcyclohexane, etc.; a divalent aromatic hydrocarbon group including all types of phenylene group, all types of methylphenylene group, all types of ethylphenylene group, all types of dimethylphenylene group, all types of naphthylene group, etc.; an alkylaromatic group to be derived from an alkylaromatic hydrocarbon such as toluene, xylene, ethylbenzene or the like, and having a monovalent bonding site both in the alkyl moiety and in the aromatic moiety therein; or an alkylaromatic group to be derived from a polyalkylaromatic

hydrocarbon such as xylene, diethylbenzene or the like, and having bonding sites in the alkyl moieties therein. Of those, especially preferred are aliphatic groups each having from 2 to 4 carbon atoms.

[0022] Examples of the divalent, ether bond oxygen-containing hydrocarbon group having from 2 to 20 carbon atoms are a methoxymethylene group, a methoxyethylene group, a methoxymethylethylene group, a 1,1-bismethoxymethylethylene group, a 1,2-bismethoxymethylethylene group, an ethoxymethylethylene group, a (2-methoxyethoxy)methylethylene group, a (1-methyl-2-methoxy)methylethylene group, etc. In formula (V), a indicates the number of the repetitive R^8O therein, and falls between 0 and 10 on average, preferably between 0 and 5. Plural R^8O 's, if any in formula (v), may be the same or different.

[0023] In formula (V), R^9 represents a hydrocarbon group having from 1 to 20, preferably from 1 to 10 carbon atoms. Concretely, the hydrocarbon group indicates, for example, an alkyl group including a methyl group, an ethyl group, an n-propyl group, an isopropyl group, all types of butyl group, all types of pentyl group, all types of hexyl group, all types of heptyl group, all types of octyl group, all types of nonyl group, all types of decyl group; a cycloalkyl group including a cyclopentyl group, a cyclohexyl group, all types of methylcyclohexyl group, all types of ethylcyclohexyl group, all types of propylcyclohexyl group, all types of dimethylcyclohexyl group, etc.; an aryl group including a phenyl group, all types of methylphenyl group, all types of ethylphenyl group, all types of dimethylphenyl group, all types of propylphenyl group, all types of trimethylphenyl group, all types of butylphenyl group, all types of naphthyl group, etc.; or an arylalkyl group including a benzyl group, all types of phenylethyl group, all types of methylbenzyl group, all types of phenylpropyl group, all types of phenylbutyl group, etc.

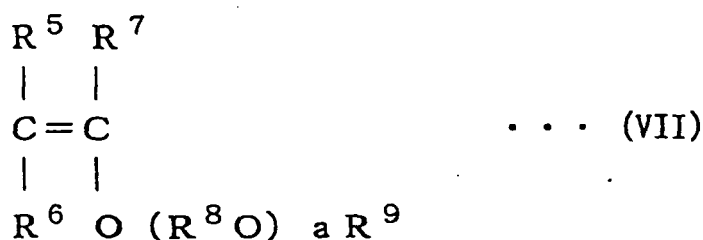
[0024] The polyvinyl ether compounds (1) have the constitutive units of formula (V), in which the number of the repetitive units (that is, the degree of polymerization of the compounds) may be suitably selected depending on the desired kinematic viscosity of the compounds. In the polyvinyl ether compounds, the ratio by mol of carbon/oxygen preferably falls between 3.5 and 7.0. If the molar ratio is smaller than 3.5, the moisture absorption of the compounds will be high; but if larger than 7.0, the compatibility of the compounds with refrigerants will be poor.

[0025] The polyvinyl ether compounds (2) are block or random copolymer having the constitutive units of formula (V) and the constitutive units of formula (VI). In formula (VI), R^{10} to R^{13} each represent a hydrogen atom, or a hydrocarbon group having from 1 to 20 carbon atoms, and they may be the same or different. For examples of the hydrocarbon group having from 1 to 20 carbon atoms, referred to are the same as those mentioned hereinabove for R^9 in formula (V). R^{10} to R^{13} may be the same or different in different constitutive units.

[0026] The degree of polymerization of the polyvinyl ether compounds (2) of block or random copolymers having the constitutive units of formula (V) and the constitutive units of formula (VI) may be suitably determined, depending on the desired kinematic viscosity of the compounds. In the polyvinyl ether compounds, the ratio by mol of carbon/oxygen preferably falls between 3.5 and 7.0. If the molar ratio is smaller than 3.5, the moisture absorption of the compounds will be high; but if larger than 7.0, the compatibility of the compounds with refrigerants will be poor.

[0027] The polyvinyl ether compounds (3) are mixtures of the above-mentioned polyvinyl ether compounds (1) and (2), in which the blend ratio of the compounds (1) and (2) is not specifically defined.

[0028] The polyvinyl ether compounds (1) and (2) for use in the invention may be produced through polymerization of vinyl ether monomers corresponding thereto, or through copolymerization of hydrocarbon monomers having an olefinic double bond and corresponding thereto with vinyl ether monomers also corresponding thereto. The vinyl ether monomers may be represented by the following general formula (VII):



wherein R^5 to R^9 and a have the same meanings as above.

[0029] Corresponding to the above-mentioned polyvinyl ether compounds (1) and (2), the vinyl ether monomers include various compounds, for example, vinyl methyl ether, vinyl ethyl ether, vinyl n-propyl ether, vinyl isopropyl ether, vinyl n-butyl ether, vinyl isobutyl ether, vinyl sec-butyl ether, vinyl tert-butyl ether, vinyl n-pentyl ether, vinyl n-hexyl ether, vinyl 2-methoxyethyl ether, vinyl 2-ethoxyethyl ether, vinyl 2-methoxy-1-methylethyl ether, vinyl 2-methoxy-2-methyl ether, vinyl 3,6-dioxaheptyl ether, vinyl 3,3,6-trioxadecyl ether, vinyl 1,4-dimethyl-3,6-dioxaheptyl ether, vinyl 1,4,7-trimethyl-3,6,9-trioxadecyl ether, vinyl-2,6-dioxa-4-heptyl ether, vinyl 2,6,9-trioxa-4-decyl ether, 1-methoxypropene, 1-ethoxypro-

pene, 1-n-propoxypropene, 1-isopropoxypropene, 1-n-butoxypropene, 1-isobutoxypropene, 1-sec-butoxypropene, 1-tert-butoxypropene, 2-methoxypropene, 2-ethoxypropene, 2-n-propoxypropene, 2-isopropoxypropene, 2-n-butoxypropene, 2-isobutoxypropene, 2-sec-butoxypropene, 2-tert-butoxypropene, 1-methoxy-1-butene, 1-ethoxy-1-butene, 1-n-propoxy-1-butene, 1-isopropoxy-1-butene, 1-n-butoxy-1-butene, 1-isobutoxy-1-butene, 1-sec-butoxy-1-butene, 1-tert-butoxy-1-butene, 2-methoxy-1-butene, 2-ethoxy-1-butene, 2-n-propoxy-1-butene, 2-isopropoxy-1-butene, 2-n-butoxy-1-butene, 2-isobutoxy-1-butene, 2-sec-butoxy-1-butene, 2-tert-butoxy-1-butene, 2-methoxy-2-butene, 2-ethoxy-2-butene, 2-n-propoxy-2-butene, 2-isopropoxy-2-butene, 2-n-butoxy-2-butene, 2-isobutoxy-2-butene, 2-sec-butoxy-2-butene, 2-tert-butoxy-2-butene, etc.

[0030] These vinyl ether monomers may be produced in any known methods.

[0031] The olefinic double bond-having hydrocarbon monomers may be represented by the following general formula (VIII):



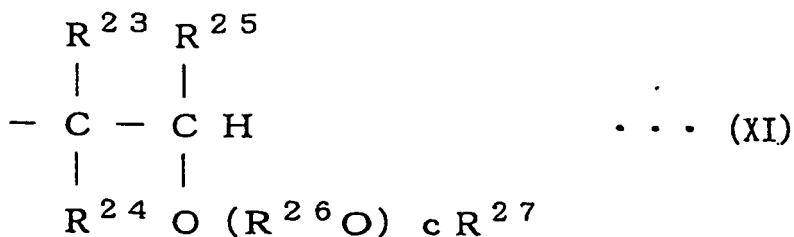
wherein R^{10} to R^{13} have the same meanings as above.

[0032] The monomers include, for example, ethylene, propylene all isomers of butene, all isomers of pentene, all isomers of hexene, all isomers of heptene, all isomers of octene, diisobutylene, triisobutylene, styrene, all isomers of alkyl-substituted styrenes, etc.

[0033] Preferably, the polyvinyl ether compounds for use in the invention are specifically terminated in the manner mentioned below. In one preferred example of the terminal structure of the compounds, one end of the molecule is terminated with a group of the following general formula (IX) or (x):



wherein R^{14} to R^{16} each represent a hydrogen atom, or a hydrocarbon group having from 1 to 8 carbon atoms, and they may be the same or different; R^{19} to R^{22} each represent a hydrogen atom, or a hydrocarbon group having from 1 to 20 carbon atoms, and they may be the same or different; R^{17} represents a divalent hydrocarbon group having from 1 to 10 carbon atoms, or a divalent, ether bond oxygen-containing hydrocarbon group having from 2 to 20 carbon atoms; R^{18} represents a hydrocarbon group having from 1 to 20 carbon atoms; b indicates a number of from 0 to 10 on average; and plural $R^{17}O$'s, if any, may be the same or different, and the other end thereof is terminated with a group of the following general formula (XI) or (XII):



wherein R^{21} to R^{25} each represent a hydrogen atom, or a hydrocarbon group having from 1 to 8 carbon atoms, and they may be the same or different; R^{28} to R^{31} each represent a hydrogen atom, or a hydrocarbon group having from 1 to 20 carbon atoms, and they may be the same or different; R^{26} represents a divalent hydrocarbon group having from 1 to 10 carbon atoms, or a divalent, ether bond oxygen-containing hydrocarbon group having from 2 to 20 carbon atoms; R^{27} represents a hydrocarbon group having from 1 to 20 carbon atoms; c indicates a number of from 0 to 10 on average; and plural R^{26} 's, if any, may be the same or different.

[0034] In another preferred example of the terminal structure of the compounds, one end of the molecule is terminated with a group of formula (IX) or (X) as above and the other end thereof is terminated with a group of the following general formula (XIII):



wherein R^{32} to R^{34} each represent a hydrogen atom, or a hydrocarbon group having from 1 to 8 carbon atoms, and they may be the same or different.

[0035] Of those polyvinyl ether compounds, the following are especially favorable for the base oil in the refrigerator oil composition of the invention.

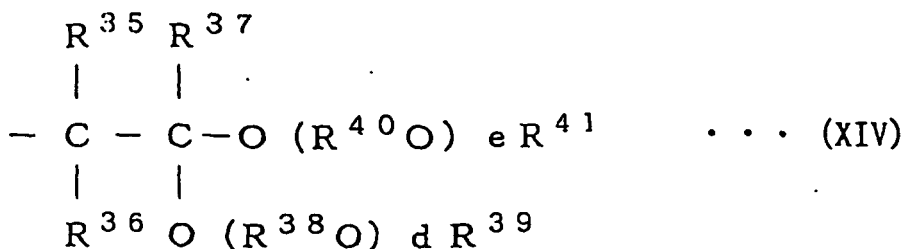
(1) Compounds comprising constitutive units of formula (v) and terminated with a group of formula (IX) or (X) at one end and with a group of formula (XI) or (XII) at the other end, in which R^5 to R^7 in the units of formula (V) are all hydrogen atoms, a is a number of from 0 to 4, R^8 is a divalent hydrocarbon group having from 2 to 4 carbon atoms, and R^9 is a hydrocarbon group having from 1 to 20 carbon atoms.

(2) Compounds composed of constitutive units of formula (v) only and terminated with a group of formula (IX) at one end and with a group of formula (XI) at the other end, in which R^5 to R^7 in the units of formula (V) are all hydrogen atoms, a is a number of from 0 to 4, R^8 is a divalent hydrocarbon group having from 2 to 4 carbon atoms, and R^9 is a hydrocarbon group having from 1 to 20 carbon atoms.

(3) Compounds comprising constitutive units of formula (V) and terminated with a group of formula (IX) or (X) at one end and with a group of formula (XIII) at the other end, in which R^5 to R^7 in the units of formula (V) are all hydrogen atoms, a is a number of from 0 to 4, R^8 is a divalent hydrocarbon group having from 2 to 4 carbon atoms, and R^9 is a hydrocarbon group having from 1 to 20 carbon atoms.

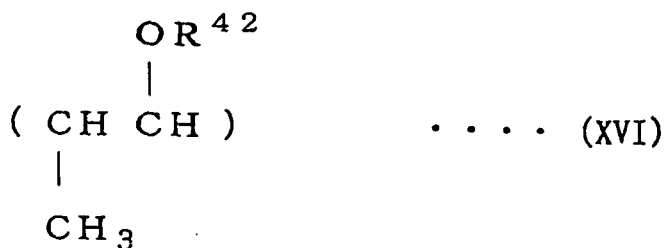
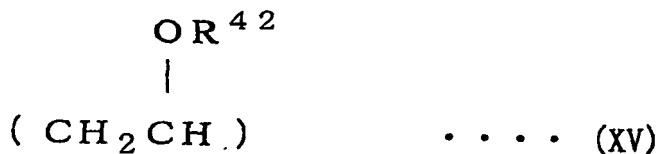
(4) Compounds composed of constitutive units of formula (V) only and terminated with a group of formula (IX) at one end and with a group of formula (XII) at the other end, in which R^5 to R^7 in the units of formula (V) are all hydrogen atoms, a is a number of from 0 to 4, R^8 is a divalent hydrocarbon group having from 2 to 4 carbon atoms, and R^9 is a hydrocarbon group having from 1 to 20 carbon atoms.

[0036] In the invention, also usable are polyvinyl ether compounds comprising the constitutive units of formula (V) and terminated with a group of formula (IX) noted above at one end and with a group of the following general formula (XIV) at the other end:



wherein R^{35} to R^{37} each represent a hydrogen atom, or a hydrocarbon group having from 1 to 8 carbon atoms, and they may be the same or different; R^{38} and R^{40} each represent a divalent hydrocarbon group having from 2 to 10 carbon atoms, and they may be the same or different; R^{39} and R^{41} each represent a hydrocarbon group having from 1 to 10 carbon atoms, and they may be the same or different; d and e each represent a number of from 0 to 10 on average, and they may be the same or different; plural $R^{38}O$'s, if any, may be the same or different, and plural $R^{40}O$'s, if any, may also be the same or different.

[0037] Further usable herein are polyvinyl ether compounds of homopolymers or copolymers of alkyl vinyl ethers, which comprise constitutive units of the following general formula (XV) or (XVI):

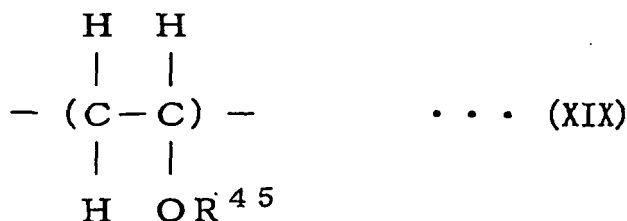


therein R^{42} represents a hydrocarbon group having from 1 to 8 carbon atoms, and have a weight-average molecular weight of from 300 to 3,000 (preferably from 300 to 2,000) and of which one end is terminated with a group of the following general formula (XVII) or (XVIII):



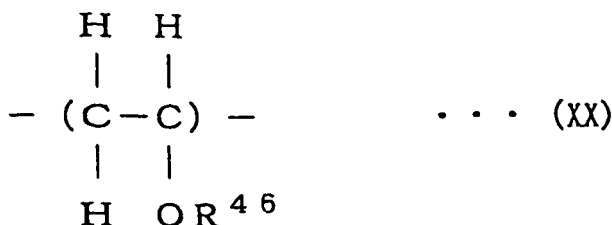
wherein R^{43} represents an alkyl group having from 1 to 3 carbon atoms; and R^{44} represents a hydrocarbon group having from 1 to 8 carbon atoms.

[0038] Especially preferred for use herein are polyvinyl ether copolymers having constitutive units (A) of the following general formula (XIX):



wherein R^{45} represents a hydrocarbon group having from 1 to 3 carbon atoms, and having or not having an ether bond in the molecule,

and constitutive units (B) of the following general formula (XX):



wherein R^{46} represents a hydrocarbon group having from 3 to 20 carbon atoms, and having or not having an ether bond in the molecule,

in which, however, R^{45} in the constitutive units (A) is not the same as R^{46} in the constitutive units (B).

[0039] In these, preferably, R^{45} is an alkyl group having from 1 to 3 carbon atoms, and R^{46} is an alkyl group having from 3 to 20 carbon atoms. More preferred are homopolymers in which R^{45} is an ethyl group; and copolymers in which R^{45} is a methyl or ethyl group, and R^{46} is an alkyl group having from 3 to 6 carbon atoms. Most preferred are copolymers in which R^{45} is an ethyl group, and R^{46} is an isobutyl group. In these, the ratio of the constitutive units (A) to the constitutive units (B) preferably falls between 95:5 and 50:50 by mol, more preferably between 95:5 and 70:50. The copolymers may be random or block copolymers.

[0040] The polyvinyl ether compounds may be produced through radical polymerization, cationic polymerization or radiation polymerization of the monomers mentioned hereinabove. For example, the vinyl ether monomers may be polymerized in the manner mentioned below to give polymers having a desired viscosity.

[0041] To initiate the polymerization, employable is a combination of any of Brønsted acids, Lewis acids or organic metal compounds with any of water, alcohols, phenols, acetals or vinyl ether-carboxylic acid adducts.

[0042] The Brønsted acids include, for example, hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, nitric acid, sulfuric acid, trichloroacetic acid, trifluoroacetic acid, etc. The Lewis acids include, for example, boron trifluoride, aluminium trichloride, aluminium tribromide, tin tetrachloride, zinc dichloride, ferric chloride, etc. Of these Lewis acids, especially preferred is boron trifluoride. The organic metal compounds include, for example, aluminium

diethylchloride, aluminium ethylchloride, diethylzinc, etc.

[0043] Any of water, alcohols, phenols, acetals or vinyl ether-carboxylic acid adducts may be selected and combined with any of the compounds mentioned above. The alcohols include, for example, saturated aliphatic alcohols having from 1 to 20 carbon atoms such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, tert-butanol, all isomers of pentanol, all isomers of hexanol, all isomers of heptanol, all isomers of octanol, etc.; and unsaturated aliphatic alcohols having from 3 to 10 carbon atoms such as allyl alcohol, etc.

[0044] In the vinyl ether-carboxylic acid adducts, the carboxylic acid includes, for example, acetic acid, propionic acid, n-butyric acid, isobutyric acid, n-valeric acid, isovaleric acid, 2-methylbutyric acid, pivalic acid, n-caproic acid, 2,2-dimethylbutyric acid, 2-methylvaleric acid, 3-methylvaleric acid, 4-methylvaleric acid, enanthic acid, 2-methylcaproic acid, caprylic acid, 2-ethylcaproic acid, 2-n-propylvaleric acid, n-nonanoic acid, 3,5,5-trimethylcaproic acid, undecanoic acid, etc.

[0045] In the adducts, the vinyl ether may be the same as or different from that to be polymerized to give the intended polymers. To prepare the vinyl ether-carboxylic acid adducts, the two are mixed and reacted at a temperature falling between 0 and 100°C or so. The product may be separated from the reaction mixture through distillation or the like and used in the polymerization of vinyl ether monomers, but may be directly used therein without being separated.

[0046] In case where any of water, alcohols or phenols is used in the polymerization, one end of the resulting polymers at which the polymerization was initiated is terminated with hydrogen. In case where an acetal is used, that one end is terminated with hydrogen or an acetal-derived group of which one alkoxy group has released from the used acetal. In case where a vinyl ether-carboxylic acid adduct is used, that one end is terminated with an alkylcarbonyloxy group derived from the carboxylic acid moiety of the vinyl ether-carboxylic acid adduct used.

[0047] On the other hand, the other end of the polymers at which the polymerization was terminated forms an acetal, olefin or aldehyde terminal when any of water, alcohols, phenols or acetals is used in the polymerization. However, when a vinyl ether-carboxylic acid adduct is used, it forms a hemiacetal carboxylate.

[0048] The terminals of the polymers thus produced may be converted into any desired groups in any known methods. The desired groups include, for example, residues of saturated hydrocarbons, ethers, alcohols, ketones, nitriles, amides, etc., but are preferably residues of saturated hydrocarbons, ethers or alcohols.

[0049] Though depending on the type of the starting material and the initiator used, the polymerization of the vinyl ether monomers of formula (VII) may be initiated at a temperature falling between -80 and 150°C, but in general, it is initiated at a temperature falling between -80 and 50°C. The polymerization finishes within 10 seconds to 10 hours or so after its start.

[0050] The molecular weight of the polymers to be produced through the polymerization as above may be controlled as follows. When the amount of any of water, alcohols, phenols, acetals or vinyl ether-carboxylic acid adducts to be in the polymerization system is increased relative to the amount of the vinyl ether monomer of formula (VII) to be polymerized, then the polymers produced may have a lowered mean molecular weight. In addition, when the amount of any of Brønsted acids or Lewis acids is increased, then the polymers produced may also have a lowered mean molecular weight.

[0051] The polymerization is effected generally in the presence of a solvent. The solvent is not specifically defined so far as it dissolves the necessary amount of the starting material and is inert to the reaction. Its preferred examples are hydrocarbons such as hexane, benzene, toluene, etc.; and ethers such as ethyl ether, 1,2-dimethoxyethane, tetrahydrofuran, etc. The polymerization may be stopped by adding an alkali to the system. After having been thus polymerized, the reaction mixture may be optionally subjected to ordinary separation and purification to thereby isolate the intended polyvinyl ether compound having constitutive units of formula (V).

[0052] As so mentioned hereinabove, the ratio of carbon/oxygen by mol in the polyvinyl ether compounds for use in the invention preferably falls between 3.5 and 7.0. For this, the molar ratio of carbon/oxygen of the starting monomers shall be so controlled that the molar ratio carbon/oxygen in the resulting polymer may fall within the preferred range. Concretely, when the ratio of the monomer having a larger carbon/oxygen molar ratio is larger, then the polymer produced has a larger carbon/oxygen molar ratio; but when the ratio of the monomer having a smaller carbon/oxygen molar ratio is larger, then the polymer produced has a smaller carbon/oxygen molar ratio.

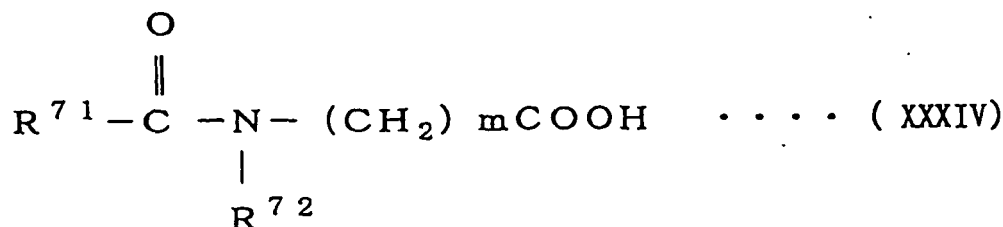
[0053] The preferred molar ratio of the polymers may also be attained by controlling the combination of the initiator selected from water, alcohols, phenols, acetals and vinyl ether-carboxylic acid adducts, and the vinyl ether monomers to be polymerized as in the above-mentioned polymerization method for the monomers. Concretely, when the initiator is selected from alcohols and phenols having a larger carbon/oxygen molar ratio than the monomers to be polymerized, then the polymers produced have a larger carbon/oxygen molar ratio than the starting monomers; but when the initiator used is an alcohol such as methanol, methoxymethanol or the like having a smaller carbon/oxygen molar ratio, then the polymers produced have a smaller carbon/oxygen molar ratio than the starting monomers.

[0054] In case where vinyl ether monomers are copolymerized with olefinic double bond-having hydrocarbon monomers, the resulting polymers have a larger carbon/oxygen molar ratio than the starting vinyl ether monomers. In this case, the molar ratio of the polymers may be controlled by controlling the proportion of the olefinic double bond-having hydrocarbon monomers to be copolymerized and the number of carbon atoms constituting the monomers.

[0055] The components (a) and (b) to be incorporated into the base oil are described.

Component (a)

[0056] The component (a) is any of organic acids of the following general formula (XXXIV):



wherein R^{71} represents an alkyl group having from 6 to 30 carbon atoms, or an alkenyl group having from 6 to 30 carbon atoms; R^{72} represents an alkyl group having from 1 to 4 carbon atoms; and m indicates an integer of from 1 to 4.

[0057] Representing an alkyl group having from 6 to 30 carbon atoms, or an alkenyl group having from 6 to 30 carbon atoms, R^{71} is preferably an alkyl group having from 10 to 20 carbon atoms, or an alkenyl group having from 10 to 20 carbon atoms. Representing an alkyl group having from 1 to 4, R^{72} is preferably a methyl group. Indicating an integer of from 1 to 4, m is preferably 1. Preferred examples of the organic acids are N-oleoylsarcosine, N-stearoylsarcosine, N-palmitoylsarcosine, N-myristoylsarcosine, N-lauroylsarcosine, etc. For the component (a), one or more organic acids mentioned above may be used either singly or as combined.

[0058] The amount of the component (a) to be in the composition falls between 0.01 and 5 % by weight based on the total amount of the composition. If it is too small, the object of the invention could not be sufficiently attained; and even if too large, it will not produce better results, and if too large, the solubility of the component (a) in the base oil rather lowers. Preferably, the amount of the component (d) falls between 0.05 and 2 % by weight.

Components (b)

[0059] Fatty acids in the fatty acid amides for the component (b) preferably have from 12 to 24 carbon atoms.

[0060] The fatty acids having from 12 to 24 carbon atoms may be linear or branched, and may be saturated or unsaturated.

[0061] Concretely, the linear saturated fatty acids include lauric acid, tridecylic acid, myristic acid, pentadecylic acid; palmitic acid, margaric acid, stearic acid, nonadecylic acid, arachic acid, behenic acid, lignoceric acid, etc.

[0062] Concretely, the linear unsaturated fatty acids include linderic acid, 5-lauroleic acid, tuduric acid, myristoleic acid, zoomaric acid, petroceric acid, oleic acid, elaidic acid, eicosenoic acid, erucic acid, selacholeic acid, etc.

[0063] Concretely, the branched saturated fatty acids include all isomers of methylundecanoic acid, all isomers of propylnonanoic acid, all isomers of methyldecanoic acid, all isomers of propyldecanoic acid, all isomers of methyltridecanoic acid, all isomers of methyltetradecanoic acid, all isomers of methylpentadecanoic acid, all isomers of ethyltetradecanoic acid, all isomers of methylhexadecanoic acid, all isomers of propyltetradecanoic acid, all isomers of ethylhexadecanoic acid, all isomers of methylheptadecanoic acid, all isomers of butyltetradecanoic acid, all isomers of methyl-octadecanoic acid, all isomers of ethyloctadecanoic acid, all isomers of methylnonadecanoic acid, all isomers of ethyloctadecanoic acid, all isomers of methyleicosanoic acid, all isomers of propyloctadecanoic acid, all isomers of butyloctadecanoic acid, all isomers of methyl-docosanoic acid, all isomers of pentyloctadecanoic acid, all isomers of methyltricosanoic acid, all isomers of ethyldocosanoic acid, all isomers of propylhexaeicosanoic acid, all isomers of hexyloctadecanoic acid, 4,4-dimethyldecanoic acid, 2-ethyl-3-methylnonanoic acid, 2,2-dimethyl-4-ethyloctanoic acid, 2-propyl-3-methylnonanoic acid, 2,3-dimethyldodecanoic acid, 2-butyl-3-methylnonanoic acid, 3,7,11-trimethyldodecanoic acid, 4,4-dimethyltetradecanoic acid, 2-butyl-2-pentylheptanoic acid, 2,3-dimethyltetradecanoic acid, 4,8,12-trimethyltridecanoic acid, 14,14-dimethylpentadecanoic acid, 3-methyl-2-heptylnonanoic acid, 2,2-dipentylheptanoic acid, 2,2-dimethylhexadecanoic acid, 2-octyl-3-methylnonanoic acid, 2,3-dimethylheptadecanoic acid, 2,4-dimethylcatadecanoic acid, 2-butyl-2-heptylnonanoic acid, 20,20-dimethylheneicosanoic acid, etc.

[0064] The branched unsaturated fatty acids include 5-methyl-2-undecenoic acid, 2-methyl-2-dodecenoic acid, 5-methyl-2-tridecenoic acid, 2-methyl-9-octadecenoic acid, 2-ethyl-9-octadecenoic acid, 2-propyl-9-octadecenoic acid, 2-methyl-2-eicosenoic acid, etc. Of the fatty acids mentioned above, preferred are stearic acid, oleic acid, 16-methylheptadecanoic acid (isostearic acid), etc.

[0065] For the component (b), one or more compounds mentioned above may be used either singly or as combined.

[0066] The amount of the component (b) to be in the composition falls between 0.01 and 5 % by weight based on the total amount of the composition. If it is too small, the object of the invention could not be sufficiently attained; and even if too large, it will not produce better results, and if too large, the solubility of the component (b) in the base oil rather lowers. Preferably, the amount of the component (e) falls between 0.1 and 2 % by weight.

[0067] The refrigerator oil composition of the invention may optionally contain, if desired, various known additives, for example, extreme pressure agents such as tricresyl phosphate, etc.; phenolic or amine-based antioxidants; acid-trapping agents such as epoxy compounds, e.g., phenyl glycidyl ether, cyclohexene-oxide, epoxidated soybean oil, etc.; copper-inactivating agents such as benzotriazole, benzotriazole derivatives, etc. ; and defoaming agents such as silicone oils, fluorosilicone oils, etc.

[0068] The refrigerants to be used in refrigerators to which the refrigerator oil composition of the present invention is applied are, for example, hydrofluorocarbons, fluorocarbons, hydrocarbons, ethers, carbon dioxide-containing refrigerants, and ammonia-containing refrigerants. Of those, preferred are hydrofluorocarbons. Preferred examples of hydrofluorocarbons are 1,1,1,2-tetrafluoroethane (R134a), difluoromethane (R32), pentafluoroethane (R125) and 1,1,1-trifluoroethane (R143a). One or more of these may be used either singly or as combined. These hydrofluorocarbons are preferred for refrigerants for compression refrigerators, as there is no possibility of their destroying the ozone layer. Examples of mixed refrigerants to which the oil composition of the invention is also applicable are a mixture of R32, R125 and R134a in a ratio by weight of 23 :25 :52 (hereinafter referred to as R407C) ; a mixture thereof in a ratio by weight of 25:15:60; a mixture of R32 and R125 in a ratio by weight of 50:50 (hereinafter referred to as R410A) ; a mixture of R32 and R125 in a ratio by weight of 45:55 (hereinafter referred to as R410B ; a mixture of R125, R143a and R134a in a ratio by weight of 44:52:4 (hereinafter referred to as R404A) ; a mixture of R125 and R143a in a ratio by weight of 50:50 (hereinafter referred to as R507), etc.

[0069] The invention is described in more detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention.

[Examples 1 and 2, Comparative Example 1 ,and Reference Examples 1 to 4]

[0070] The base oil used herein is a polyvinyl ethyl ether (a) /polyisobutyl ether (b) random copolymer [unit (a) /unit (b) = 9/1; kinematic viscosity 68 mm²/sec (40°C) ; number-average molecular weight 720]. To the base oil, added were the additives shown in Table 1 to prepare refrigerator oil compositions. In Table 1, the amount of each additive indicated is based on the total amount of the composition. The compositions were tested for their lubricity in an extreme-pressure region (hereinafter referred to as extreme-pressure lubricity) and in an oil region (hereinafter referred to as oil-region lubricity) and for their volume resistivity in the manner mentioned below. The test results are shown in Table 1.

[Extreme-Pressure Lubricity]

[0071]

Testing Machine: Falex abrasion tester

Materials: block/pin = A390 (aluminium)/AISI-3135 (steel)

Oil Temperature: room temperature

Load: 1,000 lbs (4,450 N)

Rotation: 290 rpm

Test Time: 30 min

Atmosphere: R134a (blown)

Tested Matter: abrasion loss (mm) of block

Test Method: ASTM D 2670-94

[Oil-Region Lubricity]

[0072]

Testing Machine: sealed block-on-ring tester

Materials: block/ring = A4032 (aluminium)/FC250 (cast iron)

Oil Temperature: 70°C

Load: 10 kg (100 N)

Rotation: 300 rpm

Test Time: 30 min

Atmosphere: R134a sealed (0.6 MPa)

EP 1 681 342 B1

Tested Matter: abrasion loss (mm) of block

Test Method: Proceedings of the 1998 International Refrigeration Conference at Purdue (1998), page 379 referred to.

Table 1 (1)

		Reference 1	Reference 2	Reference 3	Example 1
Blend Ratio (wt.%)	Component (a)*1	0.01	-	-	-
	Component (b)*2	-	1.0	-	-
	Component (c)*3	-	-	0.3	-
	Component (d)*4	-	-	-	0.3
	Component (e)*5	-	-	-	-
	Sorbitan Mono-oleate	-	-	-	-
	Other Additives*6	0.7	0.7	0.7	0.7
Extreme-Pressure Lubricity: abrasion loss (mm)		0.49	-	-	-
Oil-Region Lubricity: abrasion loss (mm)		-	1.3	1.4	1.5
Volume Resistivity (Ω/cm)		5×10^{13}	1×10^{13}	5×10^{13}	5×10^{13}

Table II-1 (2)

		Example 2	Comp. Ex. 1	Ref. Ex. 4
Blend Ratio (wt.%)	Component (a)*1	-	-	-
	Component (b)*2	-	-	-
	Component (c)*3	-	-	-
	Component (d)*4	-	-	-
	Component (e)*5	1.0	-	-
	Sorbitan Mono-oleate	-	0.5	-
	Other Additives*6	0.7	0.7	0.7
Extreme-Pressure abrasion loss Lubricity: (mm)		-	-	1.13
Oil-Region Lubricity: abrasion loss (mm)		1.3	1.5	2.2
Volume Resistivity (Ω/cm)		5×10^{13}	5×10^{11}	1×10^{14}
(Notes) *1: oleic acid phosphate amine salt *2: 2,4,7,9-tetramethyl-5-decyne-4,7-diol/ethylene oxide adduct *3: potassium oleate *4: N-oleoylsarcosine *5: oleamide *6: antioxidant (phenolic compound), acid-trapping agent (epoxy compound), defoaming agent (silicone compound)				

[0073] From Table 1, it is understood that the refrigerator oil compositions of the invention all exhibit good lubricity both in the extreme-pressure region and in the oil region, and their volume resistivity is low.

INDUSTRIAL APPLICABILITY

[0074] The invention provides refrigerator oil compositions of good lubricity, which are especially effective for reducing the friction in both the oil region and the extreme-pressure region in the sliding area between aluminium materials and

steel materials and which are favorable to lubricating oil for refrigerators using non-chlorine Flon refrigerants such as R134a and the like that do not bring about environmental pollution. Accordingly, the refrigerator oil compositions of the invention are applicable to all types of compressor refrigerators such as rotary-type, scroll-type and reciprocation-type compressor refrigerators.

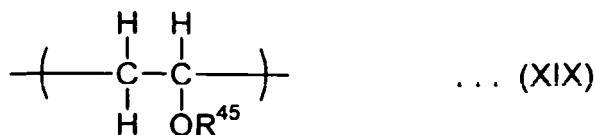
Claims

1. A refrigerator oil composition comprising as a base oil at least one oxygen-containing synthetic oil, and containing (a) at least one organic acid of the following formula (XXXIV):

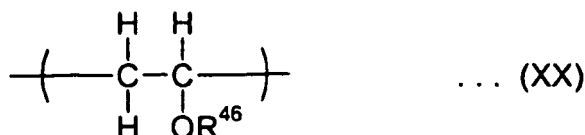


wherein R^{71} represents an alkyl group having from 6 to 30 carbon atoms, or an alkenyl group having from 6 to 30 carbon atoms; R^{72} represents an alkyl group having from 1 to 4 carbon atoms; and m represents an integer of from 1 to 4, or (b) at least one fatty acid amide, wherein the oxygen-containing synthetic oil is a polyvinyl ether.

2. The refrigerator oil composition as claimed in claim 1, wherein the amount of the components (a) or (b) falls between 0.01 and 5 % by weight based on the total amount of the composition.
3. The refrigerator oil composition as claimed in claim 1, wherein the polyvinyl ether is a polyvinyl ether copolymer having constitutive units (A) of the following general formula (XIX)



wherein R^{45} represents a hydrocarbon group having from 1 to 3 carbon atoms and optionally an ether bond in the molecule, and constitutive units (B) of the following general formula (XX)



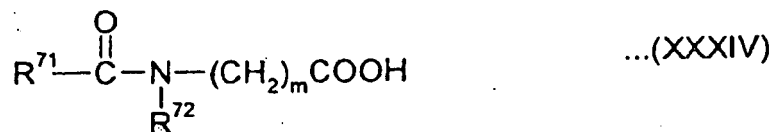
wherein R^{46} represents a hydrocarbon group having from 3 to 20 carbon atoms and optionally an ether bond in the molecule, in which, however, R^{45} in the constitutive units (A) is not the same as R^{46} in the constitutive units (B).

4. The refrigerator oil composition as claimed in claim 3, wherein R^{45} in the constitutive units (A) is an ethyl group, and R^{46} in the constitutive units (B) is an isobutyl group.

Patentansprüche

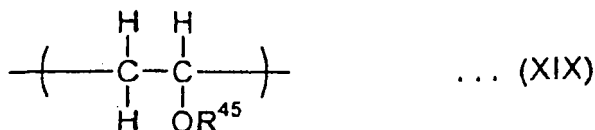
1. Kühlmaschinenölzusammensetzung, umfassend als Basisöl mindestens ein sauerstoffhaltiges synthetisches Öl,

und enthaltend (a) mindestens eine organische Säure der folgenden Formel (XXXIV):

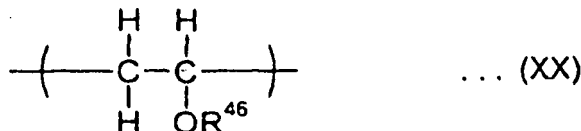


wobei R^{71} eine Alkylgruppe mit 6 bis 30 Kohlenstoffatomen oder eine Alkenylgruppe mit 6 bis 30 Kohlenstoffatomen darstellt; R^{72} eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen darstellt; und m eine ganze Zahl von 1 bis 4 darstellt, oder (b) mindestens ein Fettsäureamid, wobei das sauerstoffhaltige synthetische Öl ein Polyvinylether ist.

2. Kühlmaschinenölzusammensetzung wie in Anspruch 1 beansprucht, wobei die Menge der Komponenten (a) oder (b) zwischen 0,01 und 5 Gew.-% fällt, bezogen auf die Gesamtmenge der Zusammensetzung.
3. Kühlmaschinenölzusammensetzung wie in Anspruch 1 beansprucht, wobei der Polyvinylether ein Polyvinylethercopolymer ist, welches die Aufbaueinheiten (A) der folgenden allgemeinen Formel (XIX)



wobei R^{45} eine Kohlenwasserstoffgruppe mit 1 bis 3 Kohlenstoffatomen und gegebenenfalls einer Etherbindung im Molekül darstellt, und Aufbaueinheiten (B) der folgenden allgemeinen Formel (XX)

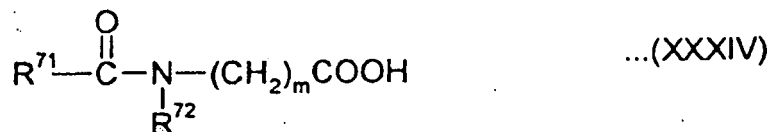


aufweist, wobei R^{46} eine Kohlenwasserstoffgruppe mit 3 bis 20 Kohlenstoffatomen und gegebenenfalls eine Etherbindung im Molekül darstellt, wobei jedoch R^{45} in den Aufbaueinheiten (A) nicht derselbe ist wie R^{46} in den Aufbaueinheiten (B).

4. Kühlmaschinenölzusammensetzung wie in Anspruch 3 beansprucht, wobei R^{45} in den Aufbaueinheiten (A) eine Ethylgruppe ist, und R^{46} in den Aufbaueinheiten (B) eine Isobutylgruppe ist.

Revendications

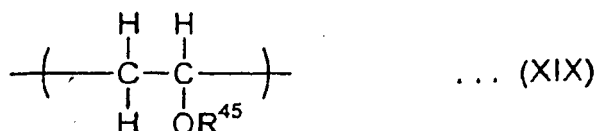
1. Composition huileuse pour machine réfrigérante comprenant en tant que huile de base au moins une huile synthétique contenant de l'oxygène, et contenant (a) au moins un acide organique de la formule suivante (XXXIV):



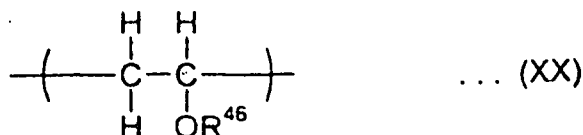
dans laquelle R^{71} représente un groupe alkyle ayant de 6 à 30 atomes de carbone, ou un groupe alkényle ayant

de 6 à 30 atomes de carbone; R^{72} représente un groupe alkyle ayant de 1 à 4 atomes de carbone, et m représente un nombre entier de 1 à 4, ou (b) au moins un amide d'acides gras, dans laquelle l'huile synthétique contenant de l'oxygène est un ester polyvinylique.

2. Composition huileuse pour machine réfrigérante selon la revendication 1, dans laquelle la quantité des constituants (a) ou (b) tombe entre 0,01 et 5 % en poids relatif à la quantité totale de la composition.
3. Composition huileuse pour machine réfrigérante selon la revendication 1, dans laquelle l'éther polyvinylique est un copolymère d'éther polyvinylique ayant des motifs constitutifs (A) de la formule générale suivante (XIX):



dans laquelle R^{45} représente un groupe hydrocarboné ayant de 1 à 3 atomes de carbone et en cas échéant une liaison étherique dans la molécule, et des motifs constitutifs (B) de la formule générale suivante (XX):



dans laquelle R^{46} représente un groupe hydrocarboné ayant de 3 à 20 atomes de carbone, et en cas échéant une liaison étherique dans la molécule, dans laquelle, cependant, R^{45} dans les motifs constitutifs (A) n'est pas le même que R^{46} dans les motifs constitutifs (B).

4. Composition huileuse pour machine réfrigérante selon la revendication 3, dans laquelle R^{45} dans les motifs constitutifs (A) est un groupe éthyle, et R^{46} dans les motifs constitutifs (B) et un groupe isobutyle.

REFERENCES CITED IN THE DESCRIPTION

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